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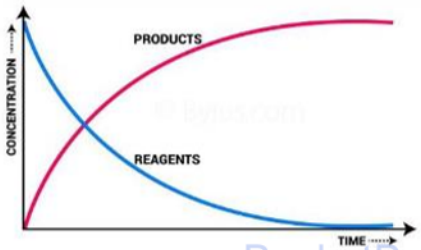
CHAPTER 8: Reaction Kinetics

Rate of reaction (RoR):



- Rate of reaction = $\frac{\Delta \text{ amount of reactants/products}}{\text{time}}$
- Rate of reaction is measured in terms of:
  - How quickly a reactant is used up
  - How quickly a product is formed
- In paper 3, rate also may be calculated by determining the inverse of time, rate = 1/time

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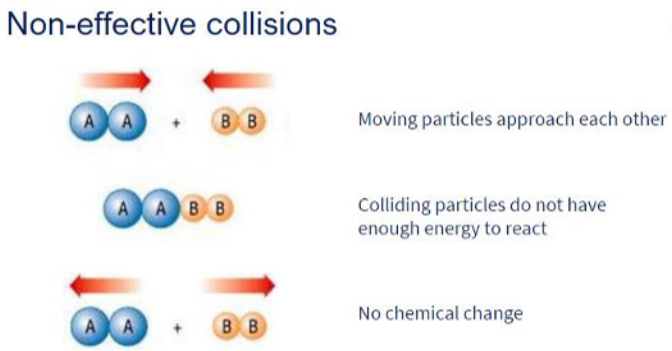
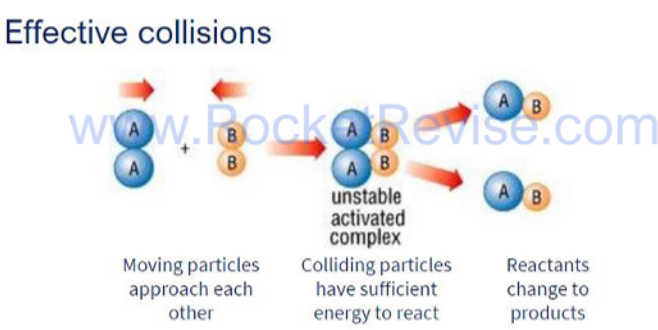
Calculating rate of reaction:

- The RoR can be determined by drawing tangents to a curve of concentration vs time
  - Initial rate of reaction
  - Rate of reaction at a given time
- The RoR is the modulus value of the tangent's gradient
  - Intial rate of reaction: gradient of tangent at t=0

Collision theory:

- The theory states that:
  - Particles must collide in the correct orientation and with sufficient energy in order to react with each other
- Chemical reactions occur due to effective collision between particles (atoms, ions or molecules)
  - Bond breaking and/ or bond formation


Non-effective collisions
Moving particles approach each other
Colliding particles do not have enough energy to react
No chemical change


Effective collisions
unstable activated complex
Moving particles approach each other
Colliding particles have sufficient energy to react
Reactants change to products

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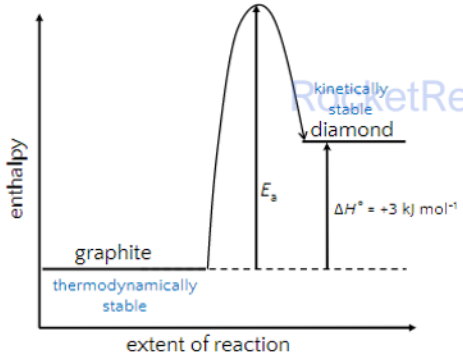
Application of collision theory:

- A reaction will speed up if:
  - The frequency of collisions increase
  - The proportion of particles with energy greater than the activation energy, E_a increases

Activation energy:

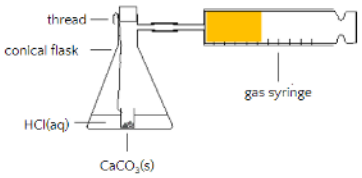
- Definition: the minimum energy required by colliding particles for an effective collision to take place



Reaction pathway diagrams / enthalpy diagrams show how the activation energy provides a barrier to reaction.

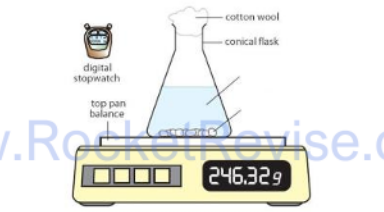
Types of experiments to measure RoR:

- Volumetric method
  - The change in volume corresponds to the amount of reactant consumed/ product formed



$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$

- Gravimetric method
  - The change in a mixture's mass corresponds to the amount of reactant consumed/ product formed



$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$

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- Calorimetric method
  - The change in a solution's colour intensity corresponds to the amount of reactant consumed/ product formed

Examples:

1. $Na_2S_2O_3$ (colourless) + $2HCl$ (colourless) → S (yellow ppt) + $SO_2 + 2NaCl + H_2O$ (colourless)

2. $S_2O_8^{2-}(aq)$ (colourless) + $2I^-(aq)$ (colourless) → $2SO_4^{2-}(aq)$ (colourless) + $I_2(aq)$

$I_2(aq) + I^-(aq) \rightarrow I_3^-(aq)$ (brown)

3. H_2O_2 (colourless) + $2I^-$ (colourless) + $2H^+$ → I_2 (Dark blue in the presence of starch indicator) + $2\,H_2O$ (colourless)

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  - Reaction of peroxydisulfate + iodide ions:
  - Over time, the intensity of t he brown solution increases with increasing I_2

$I_2(aq) + I^-(aq) \rightarrow I_3^-(aq)$ (brown)

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

- Iodometric method:
  - I^- ions + oxidising agent

H_2O_2 (colourless) + $2I^-$ (colourless) + $2H^+$ → I_2 (Dark blue in the presence of starch indicator) + $2\,H_2O$ (colourless)

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Factors that affect speed of rate of reaction:

- **Concentration**
  - At higher concentration, collisions occurm ore frequently between reactant molecules
  - This increases the rate of reaction
- **Pressure and particle size**
  - Pressure
    - Volume of the reaction vessel decrease, rate of reaction increase
  - Particle size
    - Particle size decrease, surface area increase, rate of reaction increase
- **Temperature**
  - At higher temperature, molecules have more kinetic energy
  - A higher percentage of effective collisions occur between reactant molecules → RoR increase

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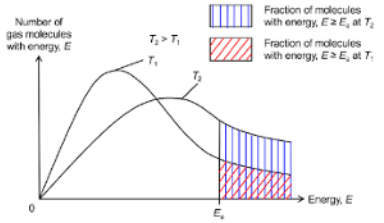
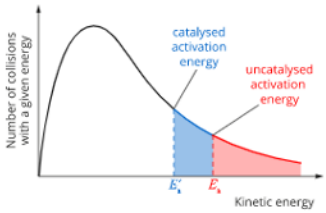

Number of gas molecules with energy, E
Fraction of molecules with energy, E ≥ Ea at T2
Fraction of molecules with energy, E ≥ Ea at T1
T2 > T1
T1
T2
0
Ea
Energy, E

Changes in Boltzmann distribution due to temperature:
at higher T, more molecules have energy greater than the E_a.

- **Catalysis**
  - Definition: a substance that increases the rate of reaction but remains chemically unchagned itself at the end of a reaction
  - A catalyst increases the rate of a reaction by providing an alternative reaction pathway with lower activation energy
  - The catalyst is not used up in the reaction
  - In the presence of a catalyst and at constant temperature
    - More molecules have sufficient energy to reaction → RoR increases



Changes in Boltzmann distribution due to catalysts:
When a catalyst is present, more molecules have energy greater than the lowered activation energy.

Types of catalysis:

- **Homogeneous catalysis**
  - The reactants and catalyst are in the same phase (either (g) or (aq))

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- Examples:
  - NO_2 catalyses production of ozone, O_3

$$O_2(g) + NO_2(g) \rightarrow \cancel{NO(g)} + O_3(g)$$
$$\cancel{NO(g)} + ½\ O_2(g) \rightarrow NO_2(g)$$

  - NO_2 catalyses production of sulfur trioxide (acid rain)

$$NO_2(g) + SO_2(g) \rightarrow SO_3(g) + \cancel{NO(g)}$$
$$\cancel{NO(g)} + ½\ O_2(g) \rightarrow NO_2(g)$$

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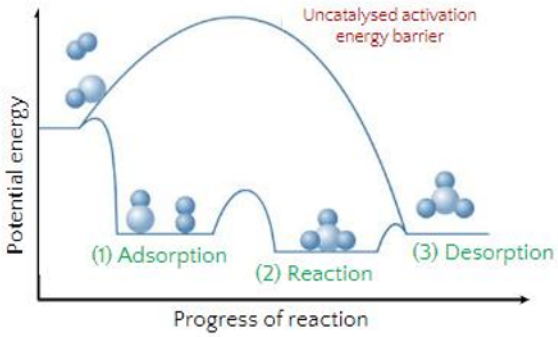
- **Heterogeneous catalysis**
  - The reactants and catalyst are in different phases
  - Mechanism of hetereogeneous catalysis:



Examples:

- Production of ammonia: Haber process
  - Catalyst: Fe

$$N_2(g) + 3H_2(g) \leftrightarrows 2NH_3(g)$$

- Production of SO_3: Contact process
  - Catalyst: V_2O_5

$$2SO_2(g) + O_2(g) \leftrightarrows 2SO_3(g)$$

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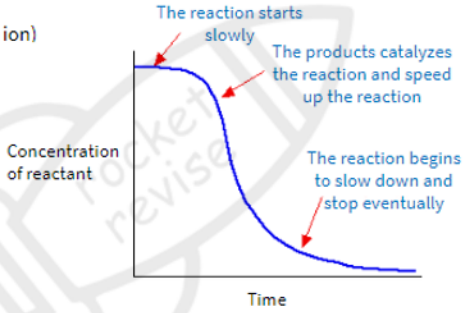
- **Autocatalysis**
  - A product of the reaction catalyses the reaction

Example:

Catalyst

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Ethanedioate ion
(common name: oxalate ion)


The reaction starts slowly
The products catalyzes the reaction and speed up the reaction
Concentration of reactant
The reaction begins to slow down and stop eventually
Time

Enzyme catalysis:

- Enzymes are proteins synthesized in nature and behave as biological catalysts
- Characteristics:
  - Enzymes are more efficient than inorganic catalysts
  - Enzymes catalyse very specific reactions
  - Enzymes do not produce byproducts
  - Enzymes work under very mild conditions

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